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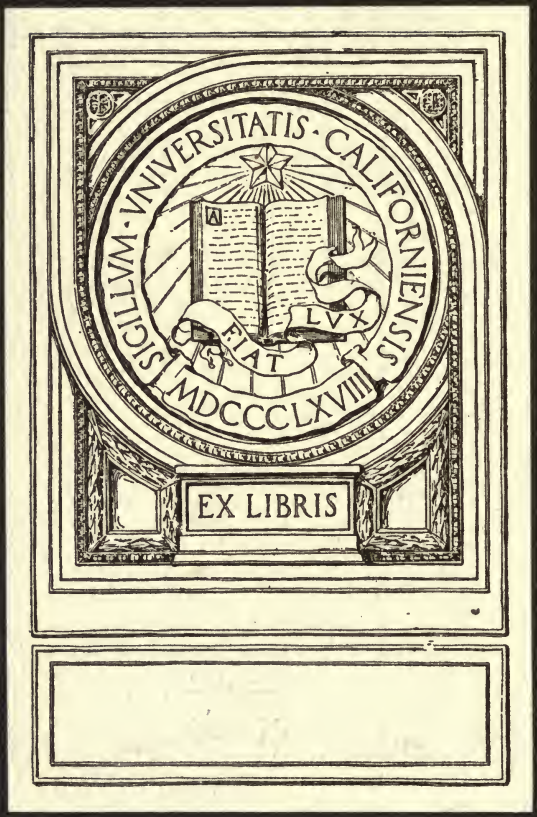
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WATER GAS AND ITS RESIDUE

By

J. C. GODBEY, A. M.

THESIS

Presented to the Faculty of Vanderbilt University for the Degree of Doctor of Philosophy

JUNE 1910

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CONTENTS

PAGE

ACKNOWLEDGEMENT 5

INTRODUCTION 7

PART I. HISTORICAL 9

Water Gas

Developement of the process of Water Gas Making.
The Present Method of making Water Gas.
The Composition of Water Gas.

The Residue in Making Gas.

The "Gas Oil".

PART II. EXPERIMENTAL 24

Comparison of the Physical Properities of the Tar and Oil.

Distillation of the Tar.
Distillation of the Oil.
Effect of Light and Air on the Fractions.
Specific Gravity
Rate of Evaporation.
Index of Refraction.
Solvents.
Effect of Lowering the Temperature.

Chemical Analysis of the Tar.

Distillation of the Tar.
Analysis of the Distillates.

The Residue.

CONCLUSIONS 48

A. I. E.

ACKNOWLEDGEMENT

This work was begun in the laboratories of Vanderbilt University, and was carried on under the supervision and with the assistance of Dr. J. T. McGill, to whom I wish to express my sincere gratitude and my appreciation of his untiring interest in my work.

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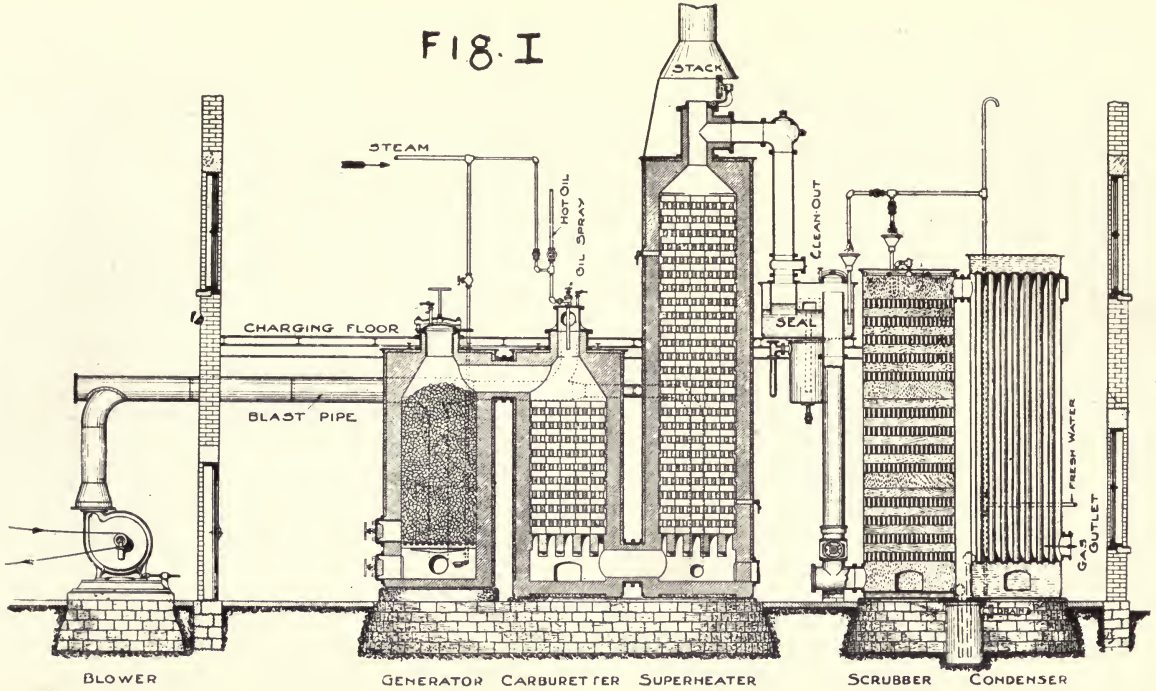
FIG. I


STACK
STEAM
HOT OIL
OIL SPRAY
CLEAN-OUT
SEAL
CHARGING FLOOR
BLAST PIPE
FRESH WATER
GAS OUTLET
DRAIN
BLOWER
GENERATOR
CARBURETTER
SUPERHEATER
SCRUBBER
CONDENSER

UNIV. OF CALIFORNIA

INTRODUCTION

The manufacture of water gas is rapidly becoming a prominent industry. As a means of lighting and heating, the gas has already been accredited an equal rank with coal gas, and bids fair to supplant it. The present system of carburetting has removed the dangers of poisoning from an odorless gas, and has also produced a yellow flame suitable for lighting purposes. It can be cheaply manufactured on a small scale as well as on a large one. The one serious drawback, however, is the comparatively useless residue which results from the process and which is known as water gas tar. Certain conditions in the manufacture of the gas result in a large yield of tar. Other conditions may produce a residue containing a high percentage of lamp black. The density of the tar seems to depend upon the kind of oil used, and the amount of tar varies according to the length of the "run." These complications and the seeming relationship existing between the oil used in the run and the residue have suggested a comparison of the physical and chemical properties of the oil and the tar.

These investigations were begun in the laboratories of Vanderbilt University in May, 1909. The material was secured at the plant of the Nashville Gas Company and was taken from time to time during a space of nine months. It consisted of a number of specimens of oil used on different days and the residue on those days. The portions used for the comparative results of the physical properties of the oil and the tar were taken at the conclusion of a day's operating to make

sure that the tar had come from a certain known oil with which it might be compared.

These precautions were taken because there seemed to be a difference in the oils used at different times. The oil used at the Nashville plant is all secured from the Standard Oil Company, and comes mostly from Indiana.

In the preparation of this paper much information has been furnishd by Mr. T. J. Cunningham, editor of the *American Gas Light Journal;* Mr. D. J. Collins, of the United Gas Improvement Company; Mr. O. O. Thwing, chief engineer of the Western Gas Construction Company; Mr. C. H. Houk, of the Standard Oil Company, and by many others.

I wish to especially thank Mr. Blake, Assistant Superintendent of the Nashville Gas Works, and Mr. Johnson, Manager of the Nashville Chemical Company, for their cooperation and assistance, and for the many courtesies extended by them during these investigations.

PART I---HISTORICAL

WATER GAS.

DEVELOPMENT OF THE PROCESS OF MAKING WATER GAS.

Water gas had its beginning in a discovery by Cavendish. In 1784 he published his conclusions that "water consists of dephlogisticated air (oxygen) united to phlogiston (hydrogen)."[1] He further demonstrated that water is decomposed by passing it over redhot charcoal. Since hydrogen was one of the resulting gases, the product of the decomposition was combustible. In the same year Mange,[2] Watt,[2], Priestley[2] and Lavoisier[2] had also experimented with the decomposition of water and had arrived at the same conclusions.

It was almost a half century later, however, before a process for making water gas was perfected and patented. In 1830, Donovan[3] patented a process for the decomposition of steam by passing it over redhot coke or charcoal. The gas was afterwards enriched with volatalized oils. Before this time several methods were employed for passing steam into coal gas retorts, but

[1]Phil. Trans., 1784, pp. 133 and 137.
[2]Life of Cavendish—Wilson.
[3]Am. Gas Lt. Journ., Vol. XLI., p. 209.

Donovan's discovery is the first process for making carburetted water gas of which we have any mention.

From 1830 to 1865 was a period of rapid development. Many different forms of apparatus were patented, and some of the processes were given practical trials. Those of Selligue,[1] Jobard,[1] White[1] and le Prince[1] probably being among the earliest of these.

The first internally fired generator was patented by George Lowe[2] in 1831. The coke was heated redhot in a retort and allowed to fall into the generator, where the heat was raised by a natural draft, the top and bottom doors being left open. The doors were then closed and steam was admitted at the top. The water gas was taken off either from the bottom or at various heights where the fire was hottest.

In 1859, Langlois[3] patented a process similar to that of Kirkham[4] (1852). Tubular retorts were used, being heated by a natural draft admitted wherever the fuel bed needed it. Steam was allowed to enter at the top and the resulting gas passed into a mixing chamber, where it was carburetted.

Schaeffer and Walcker,[5] of Berlin, took out a patent in 1860 for "a new process for the manufacture of water gas." The process, in the main, consisted of vertical retorts heated from below. The water, as steam, was admitted at the top, being decomposed as it

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[1]Wagner's Jahresbericht, Vol. V., p. 639.
[2]Am. Gas. Lt. Journ., Vol. XLI., p. 209.
[3]Wagner's Jahresbericht, Vol. V., p. 639.
[4]Jahresbericht der Chemie, Vol. 1859, p. 745; Annal de Chim. et de Phys., Vol. LI., p. 322; Polyt. Centralblat, 1859, p. 119.
[5]Journal fur Gasbebuchtung, 1862, p. 63.
Dingl. Journal, Vol. CLXIII., p. 348.
Pepert. de Chim. Appl., 1862, p. 245.
Polyt. Centralblat, 1862, p. 623, u. 657.

passed downward. It was then taken off from below and carburetted with oil.

The Fages[1] process employed the same kind of generator as the Wilkinson and was known as the "Gasogene" process. It was patented in 1860. The apparatus was installed at Narboune and produced from 1,000 to 1,200 cubic meters of gas in twenty-four hours. Gillard's[2] system was also used at Narboune, but came several years later.

In August, 1863, W. H. Gwynne[3] patented a process to be used in New York City. The steam, which was admitted at the top, was superheated by passing through pipes in the bench of double retorts. The gas was conducted directly into coal gas mains. The process was experimented with at Elizabeth, N. J.

W. H. Strong,[4] in 1877, took out a patent for a process to be used in Brooklyn, N. Y. The vertical retort was used in this system also, but the steam was admitted at the bottom and passed upward through the heated coke.

November 9, 1881, P. Jensen[5] patented a water gas apparatus in London. It consisted of one generator and two regenerators. These were heated very hot by the combustion of a portion of the water gas which had been produced. While one regenerator was thus heated, the steam was superheated in the other. The hydrocarbons were added by means of a shower of coal dust automatically regulated.

[1]Genie Industrielzeit, 1879, p. 385.
Polyt. Centralblat, 1880, p. 1101.
[2]d'Hurcourt, Deutsche Industrielzeit, 1868, p. 254.
[3]Wagner's Jahresbericht, Vol. X., p. 697.
[4]Patentschrift, December, 1877.
Deutsche Industrielzeit, 1879, p. 385.
Industriel Blotter, 1879, Vol. XXVII., p. 417.
[5]Journ. Soc. Chem. Ind., Vol. VIII., p. 533.

J. B. Archer[1] secured a patent for a new process on May 11, 1886. Steam was superheated to 1000° F. and then passed through an interjector, where it draws with it a quantity of oil. The steam and oil are then heated to 2400° F., when they are converted into permanent gas. The apparatus is composed of three concentric, cylindrical casings enclosed in brick work and having the various necessary connections.

In April, 1889, J. von Sanger and T. Cooper[2] patented an apparatus with the producers arranged in groups. These producers could be operated with soft coal. The arrangement was presumed to lower the cost of water gas.

The Tessie du Motay[3] process was one of the first practical systems. In it was introduced the "up and down run," which became a very valuable feature. The steam was decomposed in the presence of redhot coke. The "hydrogen," as the gas was incorrectly called, was stored in a tank or holder from which it was pumped into an evaporator, where it was mixed with naphtha vapors. The water gas and the vapors were then "fixed." The increase in the cost of naphtha soon made the gas too costly for practical purposes.

In 1900, J. G. T. Bormann,[4] of Berlin, patented a process in which the combustible gases were produced in a generator charged with ignited coke supplied with air enriched with oxygen. The gases were conveyed through a serpentine pipe arranged in the brick work of a chamber heated by a furnace. Steam was introduced by another similarly set pipe, both pipes being

[1]Journ. Soc. Chem. Ind., Vol. V., p. 471.
[2]Journ. Society Chem. Ind., Vol. VIII., p. 873.
[3]Zeits Angew. Chem., 1894, pp. 137-142.
Journ. Soc. Chem. Ind., Vol. XIX., p. 614.
[4]Journ. of Soc. of Chem. Ind., Vol. XXI., p. 102.

maintained at a temperature over 1200°C. This gas which entered the chamber was mainly carbon monoxide and hydrogen, the former acting with the steam to produce carbon dioxide and hydrogen. The hydrogen was drawn up into the upper part of the superheater, and then, together with the carbon dioxide, was carried to a second generator containing incandescent fuel, which received the carbon dioxide and the oxygen of the air through a grate in the side of the generator. The carbon dioxide was reduced to carbon monoxide in this generator and a gas composed mostly of carbon monoxide and hydrogen was thus formed. Part of the gas produced in the first generator was utilized to heat the oxygen-producing apparatus.

In 1902, E. Fleischer[1] patented a process for making "three quarters water gas." It had two separate blasts which were used in succession. The first produced carbon dioxide and the second carbon monoxide. Ordinary coal was used in the generator.

G. Horn[2] employed the vertical retort, but varied its height according to the kind of combustible used. It could be arranged for either finely powdered coal or a spray of oil. Superheated steam was passed through a side of the decomposing chamber, made of grating. The process was patented in May, 1903. The chief feature of the system was the continued production of water gas. Other processes having this feature were those of F. Bauke and C. Fuchs[3] (1903) and H. Koppers[4] (1901).

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[1]U. S. Pat. 701,556.
[2]Journ. of Soc. Chem. Ind., Vol. XXV., p. 1212.
[3]Fr. Pat., 329,028.
[4]Eng. Pat., 13,047.

In May, 1903, L. Guenot[1] patented an apparatus which automatically regulated the change from "make" to "blast" by the rise and fall of the gas holder. At the lower end of the producer were two inlet pipes and at the top one outlet pipe leading to a flue. These three pipes were connected by water-sealed bells attached to a lever. The rise and fall of this lever regulate the valves.

The chief feature of the Thurman[2] process (1904) is the way in which the generators are connected—in pairs during the "blast" and in series during the "make." If carburetted gas is to be made the inlet valve for the hydrocarbons is also connected to the air valve. The air and water gas which remain in the bottom of the generator and the ash pit are expelled with steam at the end of each phase.

The process almost exclusively used at the present time is the T. S. C. Lowe[3] process. He first perfected the vertical, internally-fired generator with the directly-connected carburetter and superheater and the hydraulic seal. He began his experimenting as early as 1875, and is still continuing it. The Nashville plant employs the Lowe system, which will be described fully under "The Present Method of Making Water Gas."

Opposition[4] was very bitter against water gas before 1885. It was even legislated against in some States and cities. But the present methods of carburetting and of mixing the gas in coal gas mains has

[1]Under Internat. Com., May 14, 1903.
[2]Fr. Pat., 342,578.
Journ. Soc. Chem. Ind., Vol. XXIII., p. 930.
[3]Wagner's Jahresbericht, Vol. XXV., p. 1204.
Journ. Soc. Chem. Ind., Vol. XIX., p. 614.
[4]Journ. Soc. Chem. Ind., Vol. XIX., p. 614.
Science, Vol. V., p. 303.

gradually overcome this opposition. In the year 1909 80%[1] of the gas used in the United States was water gas.

THE PRESENT METHOD OF MAKING WATER GAS.

The apparatus used in the manufacture of water gas are divided into two classes; first, those that produce the blue water gas only, which is used just as produced or carburetted separately; second, those that produce carburetted gas directly. The plant on Fourteenth Street, New York City, is an example of the former; the one at Nashville, Tennessee, employs the latter. The blue water gas system produces no residue. We will, therefore, confine the description to the carburetted water gas apparatus.

For convenience it may be divided into six parts: (1) The Gnerator, (2) Carburetter, (3) Superheater, (4) Hydraulic Seal, (5) Scrubber, and (6) Condenser. Figure I is an illustration representing these divisions and also showing the many minor parts, such as fans, sprays, drains and connections.

The Generator.—The purpose of the generator is to produce the pure water gas which burns with a non-luminous flame, or a faintly bluish one, and possesses no odor. The pure gas is simply hydrogen and carbon monoxide theoretically in equal proportions. The generator is a cylindrical steel shell of varying size and lined with a double layer of fire brick, and having a grate to support the fuel which is poured in at the top. In the side and near the bottom are doors for removing ashes and to serve as manholes when repairs are needed. The generator is filled with coke to a

[1]Sci. Am., Vol. LXLVII., p. 263.

depth of seven to ten feet. This is fired to an incandescent heat. Steam is then sprayed upon the carbon, which has a great affinity for oxygen, hence H_2 is liberated from the H_2O and C and O combine to form CO and CO_2. The amount of the CO_2 depends upon the degree of heat, depth of fuel, and amount of H_2O admitted. The per cent must be kept low since the presence of the inert CO_2 lowers th candle power and reduces the calorific value of the gas. It is generally estimated that every per cent of CO_2 reduces the power one candle.

There are three reactions that take place:

$$2H_2O+C=CO_2+2H_2.$$
$$H_2O+C=CO+H_2.$$
$$CO_2+C=CO+CO.$$

It was demonstrated by Dr. Bunte,[1] of Germany, that the reaction producing CO_2 takes place from 600° —700° C[2], and that it is only at a temperature of 1000° C that CO is formed. Hence the spray of steam must be of short duration, because it tends to lower the temperature of the coke in the generator and produce CO_2.

To restore the high temperature a blast of air is forced through the coke by means of a fan run at a regular speed. The oxygen of the air unites to form, first, CO_2, then CO as it comes in contact with the upper layer of coke. And the proportion of CO_2 again depends upon the amount of air admitted in the "blow," depth of fuel and temperature. There is always more CO during the latter part of the "blow." It is also essential that the steam be very dry so that no water

[1]Sci. Am., Vol. LXLVII., p. 263.
[2]See also Journal of the Chem. Soc., Vol. XLVIII., p. 1636.

is sprayed upon the coke to cool it. A trap for freeing the steam from water is generally employed and the pipes are well wrapped with asbestos.

The Carburetter.—In shape and size the carburetter is very much like the generator. It is filled with firebrick arranged in checker work. The gas passes from the generator into the carburetter and the heat of the "blow" is utilized to raise the temperature of the bricks. When the temperature is thus raised a spray of oil is admitted and, being vaporized, mixes with the water gas to enrich it.

The Superheater.—The superheater is very much like the carburetter and is a continuation of the "fixing" process. At its top is the stack valve, which is opened during the "blow." The superheater is heated by the same process and at the same time as the carburetter.

The Seal.—From the fixing chamber the gas passes into the seal. This is a tank of water kept hot by a continuous flow from the boiler. The gas bubbles through the hot water which serves to cool out some of the residue which settles to the bottom. The gas is somewhat cooled, also.

The Scrubber.—As the gas bubbles through the seal it passes into the scrubber. This is a cylindrical tank filled with wooden trays kept moist by a spray of water. Here the greater part of the tar-like residue is "scrubbed" out of the gas by contact with the trays. It settles to the bottom of the scrubber and is carried off by drains.

The Condenser.—The last process before purification, through which the gas passes, is the condenser. In it the gas comes in contact with rows of water-cooled

pipes which free it from any remaining tar and cool it for the relief holder. In the condenser, and also in the "washer," it loses still more of the tar and heavy oil residue. The last cleaning process is to free the gas from H_2S by passing it through a tank of iron oxide and sawdust. Finally it is carried to the relief holder and ready for distribution.

THE COMPOSITION OF WATER GAS.

Water gas varies in composition according to the process of manufacturing. Some times the gas is made and subsequently carburetted as in the Dellwick-Fleischer process[1] (1896). Usually, however, the carburetting is carried on as the gas is made. The following analyses show the composition of the gas:

1. The Dellwick-Fleischer, Uncarburetted.[2]

Carbon dioxide	4.65
Heavy hydrcarbons	.05
Oxygen	.20
Carbon monoxide	39.65
Marsh gas	.82
Hydrogen	50.80
Nitrogen	3.83

2. The Carburetted.[3]

Carbon dioxide	3.4
Illuminants	12.3
Oxygen	.5
Carbon monoxide	29.1
Hydrogen	30.3
Marsh gas	21.3
Nitrogen	3.1

[1]Am. Gas. Lt. Journ., Vol. XCI., p. 222.
Wagner's Jahresbericht, Vol. XLIII.
[2]Sci. Am., Sup. Vol. LII., p. 21706.
[3]Cci. Am., Vol. LXXXIV., pp. 39 and 102.

3. The Carburetted.[1]

Hydrocarbon vapors	1.2
Carbon dioxide	3.
Heavy hydrocarbons	12.6
Oxygen	.4
Carbon monoxide	28.0
Hydrogen	31.4
Methane	20.2
Nitrogen	3.2

THE RESIDUE IN MAKING WATER GAS.

The residue is called tar because of its resemblance to coal tar. It is, however, of a much lower specific gravity and a much less viscosity, besides many other differences.

In the process of gas-making the tar is given off at four places. First, that which cools out in the hydraulic seal; second, the portion that condenses in the scrubber; third, the part that collects in the condenser, and, fourth, that which cools out in the "purifier." In each case the cooling is carried on by means of a flow of water. A steady stream of water passes through the seal and hence there is much water in this residue; the scrubber is constantly washed with a spray of water which mixes with the condensed tar. The presence of this large quantity of water is one of the chief sources of difficulty in trying to utilize the residue or in attempting to work with it.

There is very little difference in these various residues when the process is correctly operated. That which condenses out of the seal often contains more or less of the gas oil which has gone through the process uncracked. Various means are used to detect the oil. The greatest percentage of tar comes out in the scrub-

[1]Internat. Library of Tech., Vol. XX., Sec. 52, p. 2.

ber. It collects on the wooden trays some times in such quantities as to impede the process of gas-making. As it cools it runs down into a receiver, where it is collected at the bottom of a tank from which the cooling water of the scrubber constantly overflows. Being heavier than the water, the tar sinks to the bottom. Specimens from this tank were used in the experimental part of this research.

The tar from the condenser is the same as that from the scrubber. Some little residue cools out in the purifying process, but this is contaminated with the iron and sawdust.

The character of the residue may depend largely upon two things: First, the kind of oil used in the "run"; second, the way in which the process of gas-making is regulated. If the "run" is long and the "blow" short, the quantity of tar will be large and of a lower specific gravity. It will contain more heavy hydrocarbons and more of the original oil. If the "run" is short and the blow long, the tar will be less in quantity, of a higher specific gravity and a greater viscosity. More free carbon in the form of lampblack will be present and the quality of the tar will be much inferior. The gas will also be less in quantity and poorer in quality.

The greatest of care must be exercised in determining the length of time of the "run." In some plants a specially constructed pyrometer is used to keep the temperature constant and uniform. But more often the operator depends upon his ability to judge of the temperature with the eye.

As yet very little use has been found for the tar. It is usually pumped into a tank above the furnace and

used to spray the coke with which the furnace is fed. It burns with a heavy smoky flame.

THE "GAS OIL."

The oil used to enrich water gas is a product of petroleum. It is almost universaly furnished by the Standard Oil Company, and consists of the residue which remains after the illuminating oils have been distilled off. It is a very dark, heavy oil, with the odor of lubricating oil. It is supposed to come off above 250°C, but the incomplete process of distillation leaves some of the lower boiling fractions.

Crude petroleum contains almost all of the paraffin series as follows:

Gases	*Formula*	*C*	*H*	*Boiling Point*	*Sp. Gr.*
Methane	$C H_4$	75.00	25.00	....	.559
Ethane	$C_2 H_6$	80.00	20.00	....	.5516
Propane	$C_3 H_8$	81.81	18-19	—20°C	1.522
Butane	$C_4 H_{10}$	82.80	17.20	1°C	.6(0°C
Liquids					
Pentane	$C_5 H_{12}$	83.33	16.67	37°C	.628
Hexane	$C_6 H_{14}$	83.72	16.28	69°C	.664
Septane	$C_7 H_{16}$	84.00	16.00	97.5°C	.699
Octane	$C_8 H_{18}$	84.21	15.79	125°C	.703
Nonane	$C_9 H_{20}$	84.38	15.62	136°C	.741
Decane	$C_{10} H_{22}$	84.51	15.49	158°C	.757
Undecane	$C_{11} H_{24}$	84.61	15.39	182°C	.765
Dodecane	$C_{12} H_{26}$	54.70	15.30	198°C	.776
Tridecane	$C_{13} H_{28}$	84.78	15.22	216°C	.792
Tetradecane	$C_{14} H_{30}$	84.85	15.15	238°C	.812
Pentadecane	$C_{15} H_{32}$	84.90	15.10	258°C	.825
Hexadecane	$C_{16} H_{34}$	84.94	15.06	180°C	.828
Solids					
Paramyricyl	$C_{27} H_{56}$	85.26	14.74		
Paracryl	$C_{30} H_{62}$	85.31	14.68	370°C	

It will be seen from a study of this table that the gas oil would consist chiefly of those compounds above Decane ($C_{10}H_{22}$), which are either liquids or solids

[1]Internat. Library of Tech., Vol. XX., Sec. 52.

with high boiling points. The gas oil varies in specific gravity from .770 to .859, this corresponds to the specific gravity of the compounds of the Marsh gas series above Decane. The imperfect distillation precludes a complete separation, however, hence the presence of some of the series blow 250° C.

The products of crude petroleum used commercially are:

Product.	Boiling Point
Natural gas	Gas
Rhigolene	0°C
Gasoline	50°, 70°, 98°, 110°C
Kerosene	150°, 300°C
Lubricating Oil	Above 300°C
Vaseline	Solid
Paraffine	Solid

The substances known to commerce which are contained in gas oil would be kerosene, lubricating oil, vaseline and paraffine.

The amount of oil used at a "run" varies according to the length of both the "run" and the "blow." At the Nashville Gas Company's plant about thirty-two gallons is used each time. The oil is sprayed into the carburetter after having been heated by passing through pipes incased in steam jackets. The temperature being very high in the carburetters, the oil is at once "cracked." After this instantaneous vaporization it passes on through the various phases of the process.

The table on the adjoining page is a facsimile of a daily report at the gas works and is printed by the permission of the Nashville Gas Company. It shows the time consumed in the "run" and in the blow," the amount of oil used each time, the frequency with which the generator is fired with coke. Thirty-eight pounds of coke and four gallons of oil are used to pro-

duce 1,000 feet of gas. A daily run will produce 400,000 feet of gas and 750 gallons of tar. The tar varies, however, from twelve to fifteen barrels.

This report would show better results if the plant were running steadily every day. According to the present system it is operated only when the supply of coal gas is getting short and a quick replenishing of the holder is needed.

Nashville Gas Company

DAILY OPERATING REPORT

Gas Maker..... *Machine No.*..... *Date*.....

Run No.	Blast on	Min. Blow	Blast off Steam on	Min. Run	Steam Off	Oil Used	Coke Used	Min Coaling	Min Cleaning	Up or Down Run	C. P.	Oil Meter Index	Station Meter	Relief Holder	Gas Made
1	10.05	62	11.07	6	.....	...	14	...	...	...	...	583510	.....	.....	.....
2	11.13	5	11.18	6	11.24	...	6	2	...	...	...	583542	.....	.....	.....
3	11.26	12	11.38	6	.....	...	...	...	...	...	...	583574	.....	.....	.....
4	11.44	5	11.49	6	.....	...	...	...	...	...	...	583606	.....	.....	.....
5	11.55	5	12.00	6	12.06	...	3	2	...	...	...	38	.....	.....	.....
6	12.08	8	12.16	6	.....	...	...	...	...	...	...	70	.....	.....	.....
7	12.22	5	12.27	6	.....	...	...	...	...	...	...	702	.....	.....	.....
8	12.33	5	12.38	6	.....	...	...	...	...	...	...	734	.....	.....	.....
9	12.44	5	12.49	6	.....	...	...	...	...	...	...	768	.....	.....	.....
10	12.55	5	1.00	6	.....	...	...	...	...	...	...	800	.....	.....	.....
11	1.06	5	1.11	6	.....	...	...	...	...	...	...	832	.....	.....	.....
12	1.17	5	1.22	6	1.28	...	4	2	...	...	...	864	.....	.....	.....
13	1.30	8	1.38	6	.....	...	...	...	...	...	...	896	.....	.....	.....
14	1.44	5	1 49	6	.....	...	...	...	...	...	...	583930	.....	.....	.....
15	.....	...	.....	...	.....	...	...	...	...	...	...	...	.....	.....	.....
16	.....	...	.....	...	.....	...	...	...	...	...	...	420	.....	.....	105000

PART II---EXPERIMENTAL

COMPARISON OF THE PHYSICAL PROPERTIES OF THE TAR AND OIL.

DISTILLATION OF THE TAR.

One of the hindrances attendant upon the analysis or utilization of water gas tar is the very great difficulty with which it is distilled. The excessive amount of water always present must be gotten rid of to prevent serious frothing or "bumping" which causes the undistilled liquid to be carried into the delivery tube. Probably the best way to remove the water is to allow the tar to stand some time until the greater part has separated from the water which can be decanted. The tar used in the following tests was allowed to remain thirty days. When the supernatant liquid had been decanted the tar was shaken up with calcium chloride and put aside for forty-eight hours.

The flask used in the distillation of the tar, and also the oil, was a 600 cc. round bottomed distilling flask with the delivery tube near the top of the neck. The flask is preferable to the retort, because of a better fractionation of the low boiling portion of the tar.

The best burner for heating is a Bunsen flat burner which can be easily raised or lowered. This furnishes uniform heat over the bottom of the flask and can be regulated to heat gently or to a very high degree.

The flask was enclosed in an asbestos jacket and

rested upon a wire gauze coated with asbestos paste except a hole of two inches in the center. This prevented the radiated heat from affecting the thermometer.

The thermometer was placed with the bulb just below the side delivery. The upper portion was encased in a glass jacket to prevent any draft from affecting it.

Six fractions of both the oil and the tar were taken as follows:

1. Up to 160°C.
2. 160° to 200°C.
3. 200° to 260°C.
4. 260° to 310°C.
5. 310° to 340°C.
6. 340° to 360°C.

Repeated separations at various temperatures seemed to indicate these as logical points for the fractionating.

An effort was made to complete each fraction as nearly as possible. The flame was so regulated that the distillate came over at the rate of 1-2 drop a second. When nearing the completion of a fraction the drops were diminished to one every ten seconds, and finally ceased altogether. The temperature having fallen several degrees, was then gradually raised to the original. This was done several times with each fraction.

DISTILLATION OF THE OIL.

The same precautions were observed in distilling the oil as were taken with the tar. Exactly the same conditions were maintained in each case and the fractions of the one made to correspond to those of the other. The oil distilled very quietly and rapidly.

The tables given below show the results of these distillations:

The tar, 125.5 grams.

Fraction	Range in Temp.	Amt. in Grams	Percentage
1. Up to	160°C	5.76	4.60
2. 160°	200°C	3.46	7.36
3. 200°	260°C	29.38	30.73
4. 260°	310°C	29.32	50.94
5. 310°	340°C	12.19	60.67
6. 340°	360°C	14.04	71.88
7. Residue		35.10	28.12
Total		125.25	100.00

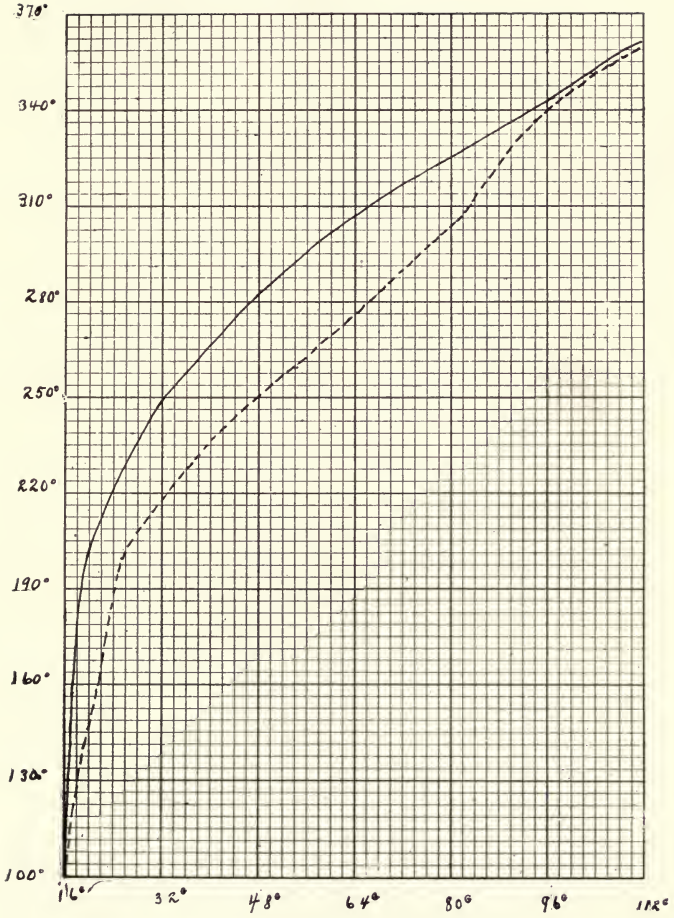
The oil, 125.5 grams.

Fraction	Range in Temp.	Amt. in Grams	Percentage
1. Up to	160°C	1.68	1.35
2. 160°	200°C	2.64	3.46
3. 200°	260°C	17.56	17.49
4. 260°	310°C	31.29	42.48
5. 310°	340°C	26.25	63.40
6. 340°	360°C	15.96	76.15
7. Residue		29.77	23.85
Total		125.15	100.00

The graph on the adjoining page shows a comparison of the curves which these fractions may be made to represent, the tar by the broken line and the oil by the solid one.

EFFECT OF LIGHT AND AIR ON THE FRACTIONS.

All of the fractions of the tar change in color upon long standing; the higher boiling ones becoming very dark. Two sets were placed under the same conditions, the one being hermetically sealed and as free from air as possible, the other loosely stoppered. Very little change took place in the distillates hermetically sealed while the other darkened. Two sets were again taken


370°
340°
310°
280°
250°
220°
190°
160°
130°
100°
16°
32°
48°
64°
80°
96°
112°

and the one placed in the light and the other in a very dark place, both sets being loosely stoppered. They became equally dark upon standing.

Some of the distillates were hermetically sealed with only a small quantity of the distillate in a large bottle, the air having been left in the bottle. These darkened also. We are thus led to conclude that the coloration is due to oxidation from the air and not to a change in the structure brought about by the action of light.

SPECIFIC GRAVITY.

The specific gravity of the tar after it had been dehydrated was found to be 1.0429 at 21.6° C. The specific gravity of the oil was .8590 at 21.6° C., water at 21.6° being taken as a standard.

RATES OF EVAPORATION.

In order that a comparison of the rate of evaporation might be made, specimens of the tar and the oil were placed in open beakers on a sand bath at 88° C. and allowed to evaporate for six hours. The oil lost 6.05% and the tar 18.47% by weight at the end of that time. The tar has increased in specific gravity .042, while the increase of that of the oil was very slight. The loss in weight of the tar seemed to be due to the elimination of water held in suspension, moisture having been collected on a watch glass held above the beaker.

INDEX OF REFRACTION.

The Abbey method was used for taking the index of refraction of the tar and the oil and also their fractions.

The following tables show a comparison of these results:

Fraction	Range in Temp.	Index of Refraction at 19.5°C	
1. Up to	160°C	1.5137	1.4333
2. 160°	200°C	1.5109	1.4374
3. 200°	260°C	1.5636	1.4613
4. 260°	310°C	1.5837	1.4781
5. 310°	340°C	1.6215	1.4837
6. 340°	360°C	1.6558	1.4918
Original "Gas Oil"			1.4809
Dehydrated tar			1.6693

Fraction	Range in Temp.	Index of Refraction at 40°C	
1. Up to	160°C	1.5037	1.4242
2. 160°	200°C	1.5097	1.4291
3. 200°	260°C	1.5549	1.4537
4. 260°	310°C	1.5759	1.4613
5. 310°	340°C	1.6141	1.4769
6. 340°	360°C	1.6477	1.4849
Original Gas Oil			1.4887
Dehydrated tar			1.6761

SOLVENTS.

The following solvents were used in which to test the solubility of the fractions of the tar and the oil: Carbon bisulphide, carbon tetrachloride, benzol, cuminol, acetone, petroleum, ether, paraffin oil, acetic acid and water. 1 g. was dissolved in 1 cc. of the solvent. The various results are shown in the table.

SOLVENT	SOLUBILITY		COLOR OF SOLUTION		RESIDUE	
	TAR	OIL	TAR	OIL	TAR	OIL
Water	insoluble	insoluble				
Carb. bisulphide	very soluble	very sol.	black reddis tinge	clear	none	none
Carb. tetrachloride.	soluble	very sol.	very dark	light brown	none	none
Benzine	soluble	very sol.	jet black	clear	brownish	none
Acetone	partially	partially	dark reddish	very clear oily residue	rather lge. brown	oily
Cuminol	soluble	soluble	dark reddish	clear	large dark brown	none
Petroleum Ether	soluble	soluble	reddish black	clear	brown	none
Parafine Oil	soluble	soluble	reddish brown	clear	black	none
Acetic Acid	part. soluble	soluble	very dark	clear	slight black	none

The various solutions were stoppered and set aside for thirty-six hours. The carbon bisulphide in which the oil had been dissolved became brownish to a slight degree, while the tar solution had become black. When filtered the filtrate came through black.

The carbon tetrachloride-oil solution had also deepened in color, and the tar solution had become black, filtering black also.

The benzine in which the oil had been dissolved changed from a clear solution to a brown; that in which the tar was dissolved became a deep black with a reddish hue. It filtered black.

The cuminol-oil solution also changed from a clear to a brown.

The tendency of all the solutions of both the oil and the tar was to darken upon standing. The tar, however, showed a more decided tendency to deepen in color. All of the tar solutions are a deep red or reddish black, while most of the oil solutions are either clear or only slightly brown.

Upon filtering the tar solutions the filtrate remains a very deep color, showing that the coloration is not due to particles of carbon held in suspension. This conclusion is verified by the deepening of the color upon long standing rather than a settling out of the carbon as a precipitate should it have been held in suspension.

EFFECT OF LOWERING THE TEMPERATURE.

An apparatus for surrounding the tar or the oil with ice and salt was prepared (see Fig. III) as follows: An inverted bottle (a) having the bottom cut off was used as the outer jacket; a long, parallel-walled

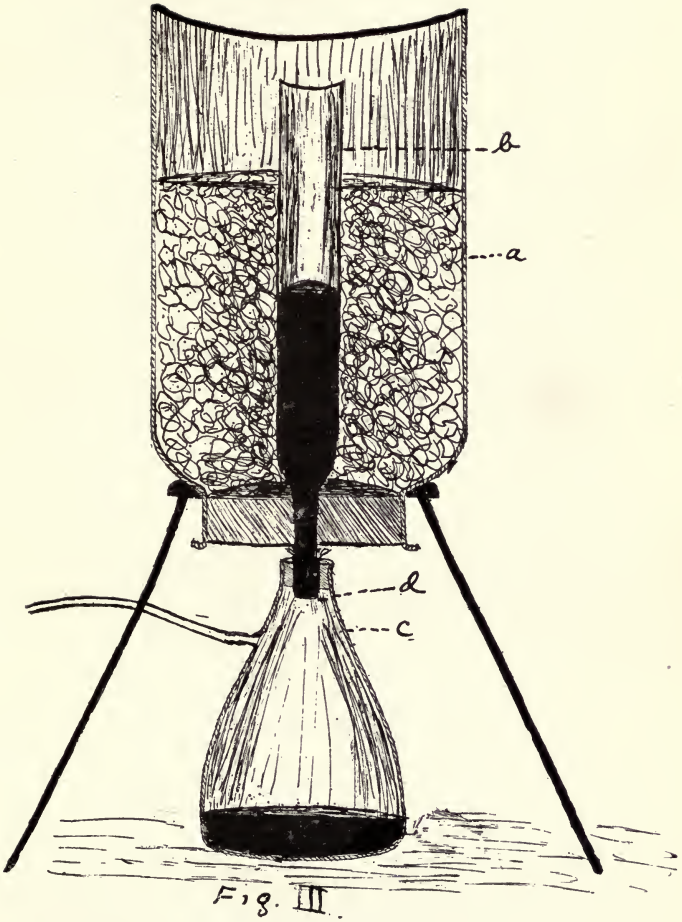


Fig. III.

funnel (b) was inserted through the stopper; the lower end was connected with an aspirator; (c) over the end of the funnel was placed a filtering cloth; (d) when the temperature of the liquid had been lowered a gentle pressure was exerted by means of the aspirator pump.

The temperature thus obtained was not sufficiently low to cause a distinct separation of solids from either the tar or the oil. At 0° C. the tar was unaffected, but the oil had become viscid. At -4° C. the tar was still unaffected, while the oil had congealed to a semi-fluid mass. At -12° C. the tar showed a slight change. The oil, however, had frozen solid and would not spill from an inverted vessel. A slight pressure was then exerted by means of the aspirator and an unsolidified liquid was forced out. A comparative test of this liquid and the frozen portion in the funnel showed no difference in specific gravity nor index of refraction.

The various distillates of the tar and oil were then placed in a mixture of salt and ice at -8° C. All of the fractions of the tar remained unaffected. I., II., III. and IV. of the oil were also unaffected, but the higher boiling fractions, V. and VI., froze solid.

CHEMICAL ANALYSIS OF THE TAR.

ANALYSES ON RECORD.

Lieberman and Burg[1] passed the heavy oils of petroleum through iron tubes heated redhot and obtained hydrocarbons of the aromatic series. They also attempted to show a similarity between these hydrocarbons and coal tar. Experimenting along the same lines

[1]Berichte der deut. Chem. Gesel, 1878, p. 273.

Salzman and Wichelhaus[2] later came to the same conclusion.

L. Premier[3] treated paraffin residues and certain fractions of petroleum coming off at a very high temperature with bromine and found that these high boiling products readily absorbed bromine and contained aromatic hydrocarbons.

Matthews and Gouldon,[4] in an analysis of the tar from water gas carburetted with Russian oil, obtained the following results:

Benzine	1.19%
Toluene	3.83%
Light Paraffine	8.51%
Solvent Naphtha	17.96%
Phenols	Trace
Middle Oils	29.14%
Creosote Oils	24.26%
Napthalene	1.28%
Anthracene (crude)	0.93%
Coke	9.80%
Total	96.90%

In 1882, Dr. A. H. Elliott[1] began an analysis of water gas tar from gas carburetted with naphtha. He found a large percentage of naphthalene and 2.63% of anthracene, but mentions no other constituents. The following table shows the result of his distilation:

Temperature degrees Celsius	Weight of Distillate from 100 Volumes	
80-200	9.2	1-3 Oil
		2-3 Solid
200-270	11.2	Solid
		17.7 Oil
270, Pitch	6.0	Solid
		26.5 Oil
Last Fraction	1.7	Semi-solid
		6.0 Oil
Total	78.3	

[1]Am. Chem. Journ., Vol. VI., p. 248.
[2]Berichte der deut. Chem. Gesel, 1878, p. 431.
[3]Am. Chem. Phys., Vol. XVII., p. 5.
Journ. Chem. Soc., Vol. XXXVI., p. 1025.
[4]Gas World, Vol. XVI., p. 625.

The naphtha used to enrich the gas from which the tar comes in the above analysis is that fraction of petroleum which comes over below 150° C. In the present system of carburetting the oil used is the fraction above 250° C. It is that portion of crude petroleum which remains directly after the illuminating oil distillate has been taken. This oil is known to commerce as gas oil, and is used at the Nashville Gas Works.

DISTILLATION OF THE TAR.

In order that larger quantities of the various fractions of the tar might be obtained for experimental purposes, a number of distilations were conducted at the works of the Nashville Chemical Company. A fourteen-gallon still was provided and so arranged that the flames could heat the sides and bottom uniformly. A hole was bored in the top, in which was inserted a glass tube sealed at the lower end. In this tube the thermometer was placed. The still was also provided with a condenser and a long delivery tube.

In the final distillation, the fractions of which will be referred to in this discussion, the following fractions were taken:

I. Up to 160°C.	V. 265°-295°.
II. 160°-210°.	VI. 295°-335°.
III. 210°-245°.	VII. 335°-365°.
IV. 245°-265°.	VIII. 365° solid.

Water was found to be present in fractions I. and II., but only traces above that, the total percentage being between 8.6% and 9%. In former distillations with inferior material as much as 19.3% to 20% of water was found to be present and came over with almost every fraction.

The water was always decanted before the tar was placed in the still, but some of it was held in suspension. This was liberated only upon heating strongly. Douglas[1] succeeded in dehydrating the tar by heating it in a closed boiler under ten atmospheres pressure, leaving only 1% of moisture.

27.27 liters of the tar were placed in the still and the heating was carried on very slowly at first. The flow from the delivery was kept uniform. Toward the last the water in the condenser was drawn off so that the higher boiling oils would come over freely. The total time consumed in the distillation was nine hours.

The following table gives the results of the distillation on the larger scale:

Fraction	Range in Temp.	Specific Gravity	Amt. in Cubic Centimeters	Percentage
Water		1.0020	2350	8.62
1. Up to	160°C	.8854	1900	6.61
2. 160°	210°C	.9219	2350	8.62
3. 210°	245°C			
4. 245°	265°C	.9624	2600	9.53
5. 265°	295°C	.9795	2500	9.16
6. 295°	335°C	.9940	3650	13.38
7 335°	365°C	1.0342	3700	13.57
Residue			5850	21.45
Total			25900	90.95

ANALSIS OF THE DISTILLATES.

The Water.

The water which came over in fractions I. and II. was separated from the tar distillate by means of a separatory funnel. When thoroughly freed from tar

[1]Journal of Gas Lighting, 1891, p. 1130.

it had a faint greenish blue color, a weak alkaline reaction, and a specifis gravity of 1.0020 at 28° C., water at 28° being taken as the standard. A small quantity was warmed with NaOH in a closed flask with a small delivery tube. An ammoniacal odor was detected and red litmus was turned blue. 500 cc. of the water was acidulated with hydrochloric acid and allowed to stand for twenty-four hours. At the end of that time a deep blue precipitate had settled out. This was filtered, washed with water containing a few drops of hydrochloric acid and the precipitate dried at 100° C. A portion of the precipitate fulfilled the following test for ferric-ferrocyanide $Fe_4(FeCy_6)_3$, Prussian blue. It is soluble in concentrated acids but reprecipitated upon dilution;[1] soluble in ammonium tartrate;[2] soluble in oxalic acid, but entirely reprecipitated when exposed for a time to sunlight.[3] When strongly heated it glows and is reduced to ferric oxide, Fe_2O_3.[4] It is insoluble in water, alcohol and dilute acids.[5]

These tests were further confirmed by subjecting the brownish residue which remained after the precipitate had been heated to redness, to the following; dissolved in hydrochloric acid and a portion tested with potassium ferrocyanide; a deep blue color. Another portion was tested with potassium-sulpho-cyanide; a red color. A third portion was made alkaline with ammonium hydroxide; a deep blue color. These prove the base to be iron. A portion of the precipitate was

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[1]Watt's Chem. Dic., Vol. II., p. 289.
[2]Berichte der deut. Chem. Gesel, Vol. VIII., p. 1503.
[3]Berichte der deut. Chem. Gesel, Vol. III., p. 12.
[4]Watt's Chem Dis,, Vol. II., p. 289.
[5]Ibid.

subjected to Lassaigne's test[1] for nitrogen, sulphur and the Halogens Nitrogen was the only one found to be present.

Besides the ferric-ferrocyanide there may be present ferrous ferrocyanide and ferrous-ferricyanide, since ferric salts oxydise ferro- to ferri-cyanides, while ferrous salts reduce ferri- to ferro-cyanides.[2]

A small amount of cyanogen which is probably present in the gas as hydrocyanic acid, acts upon the oxide of iron, formed by the action of the oxygen on the sides of the generator and carburetter, to produce iron cyanides. This cools out in the scrubber and hence is found in the tar.

The filtrate was then evaporated to dryness and left a brownish residue. A portion of this was heated to redness on a platinum foil. It burned with no flame and left a brownish red residue which was tested for inorganic substances and found to be ferric oxide, Fe_2O_3, and ferric chloride, Fe_2Cl_6.

In an analysis of the gas from the gas plant iron was found to be present,[3] probably in the form of iron carbonyl, FeCO, or iron pentacarbonyl $Fe(CO)_5$. Iron carbonyl has also been found in water gas and coal gas which has been compressed in iron cylinders.[4] The existence of a volatile compound of iron has been known since 1891, in which year it was discussed by Dr. F. Quincke before the British Chemical Society.[5] When iron is brought in contact with hydrogen gas and then treated with carbon monoxide the issuing gas is found to contain iron. When this gas comes in

[1]Carbon Compounds—Weston, p. 3.
[2]Berichte der deut. Chem. Gesel, Vol. VIII., p. 1503.
[3]Analysis of Dr. W. H. Hollinshead, 1909.
[4]Proc. Chem. Soc., 1891, p. 126.
[5]Journ. Chem. Soc., 1891, Vol. LIX., p. 604.

contact with aliphatic oils the iron compound is partially absorbed, but is decomposed upon exposture to the air, with a separation of iron hydroxide.[1] Furthermore, a trace of iron-tetra-carbonyl, Fe C_4O_4 has been found in mineral oils.[2] Iron hydroxide being soluble would appear in the filtrate of the water as an iron chloride.

A portion of the residue from the evaporated filtrate was partly dissolved in absolute alcohol. After standing a few days the alcohol evaporated, leaving a brownish colored residue. Cubical crystals separated out of a water solution of this brownish residue. These when burned gave off a vapor and seemed to indicate the presence of an organic base which has not yet been determined.

Fraction I., —— — 160° sp. gr. .8854, 6.61%.

500 cc. of fraction I. was dried with calcium chloride and refractionated, using the hempel three-bulb tube and completing each fraction as in the distillations on a small scale.

	Fraction	Range in Temp.	Amt. in C. C.
1.	60°	100°C	65
2.	100°	120°C	93
3.	120°	160°C	184
	Residue above	160°C	158

These fractions were again refractionated, giving the following results:

Fraction 1:

	Fraction	Range in Temp.	Amt. in C. C.
a.	60°	80°C	2
b.	80°	85°C	27.5
c.	85°	100°C	20
	Above	100°C	15.5

[1]Journ. Chem. Soc., Vol. LIX., pp. 605 and 1090; Treatise on Chem., Roscoe and Schorlmner, p. 1019.

[2]Journ. Chem. Soc., Vol. LIX., p. 1093.

Fraction 2+ residue from 1.			
a.	85°	100°C	35
b.	100°	105°C	10
c.	105°	115°C	40
d.	115°	120°C	22
	Above .....120°C		1.5
Fraction 3+ residue from 2.			
a.	120°	130°C	57.5
b.	130°	150°C	83
c.	150°	160°C	10
	Above	160°C	32

Fractions 1a and 1b were tested for carbon bisulphide according to the method devised by Nickels.[1] A portion of the distillate was treated with a solution of potassium hydroxide in absolute alcohol (1 g. in 20 cc) and the mixture agitated thoroughly. But no potassium xanthate, $K_2C_2H_5(CO)S_2$, separated out nor did the solution become yellow.

Thiophene,[2] C_4H_4S.

Fraction 1b was tested for thiophenes by means of the indophenin reaction.[3] The mixture of isatin and strong sulphuric acid was turned blue, indicating a trace of thiophene. If present in larger quantities the color would have been a brown. This reaction is also characteristic of thiophenic acid, C_4H_3 SCOOH, or derivatives of thiophene.

Benzene, C6H6, b. p. 80°-82°.

Fractions 1b, 1c and 2a were treated with benzene as follows:[4] Thoroughly agitated with concentrated sulphuric acid, keeping thoroughly cooled, until fresh

[1]Chem. News, Vol. XLVIII (1881), p. 148, 250.
Ibid, Vol. L (1885), p. 170.
[2]Berichte der deut. Chem. Gesel, Vol. XVI., p. 1465.
Coal Tar and Ammonia, Lunge, p. 190.
[3]Commercial Organic Anal., Allen, Vol. II., ph. 2, p. 164.
[4]Ibid, Vol. II., part 2, p. 157.

quantities of the acid are not blackened upon continued shaking. Wash with water and sodium hydrate. Again wash and dry with calcium chloride. Distill and collect the portion which comes over below 90° separately. This fraction was redistilled and almost the entire fraction came over at 80°-82°. The fractions were then cooled to 0° C., and this one froze solid. A few drops of this distillate were mixed with 1 cc. of nitric acid (sp. gr. 1.42) and 1 cc. of sulphuric (sp. gr. 1.84) and heated to boiling for thirty seconds. The mixture was poured into cold water, filtered, washed with alcohol and crystallized from alcohol in fine, nearly white needles, which melted at 89.50°, the melting point of dinitro benzene.[1]

When treated with concentrated H_2SO_4 fraction 1b lost 67% by volume, while fractions 1c and 2a lost nearly 90%. 16 cc. of benzene, m. p. 80°-82° was obtained from 500 cc. of fraction I., being 0.22% by volume of the tar.

Toluene, C_7H_8, b. p. 111°.

Fractions 2a, 2b and 2c were thoroughly agitated with concentrated sulphuric acid till fresh acid was no longer darkened, washed with water and sodium hydroxide and dried over calcium chloride and redistilled.[2] The portion from 110°-112° was collected separately. The fractions were risdistilled and cooled to 0° C., but no sign of congealing or crystallization appeared after standing twenty-four hours at this temperature. Three drops of the hydrocarbon were mixed with 1.5 cc. of fuming nitric acid and 1.5 cc. of fuming sulphuric

[1]Ident. of Pure Organic Comp., Mulliken, p. 200.
[2]Coal Tar and Ammonia, Lunge, p. 623.

acid. After thirty seconds the reaction mixture was poured into cold water, filtered, washed with alcohol and recrystallized from alcohol in nearly white needles, which melt at 70.5° C., which is the melting point of dinitrotoluene.[1]

When treated with concentrated sulphuric acid fraction 2c lost 66.3% by volume. 2a and 2b lost 95%. 8.8 cc. of toluene was gotten from 500 cc. of distillate 1, or a total of .11% of the tar is toluene.

Xylene,[2] C_8H_{10} b. p. 138°-142°.

Fraction 3b was treated with 120% of concentrated sulphuric acid and shaken up for thirty minutes. It was then washed with sodium hydroxide and water, dried over calcium chloride and redistilled. Para-xylene[3] being insoluble in cold concentrated sulphuric acid is unattacked but the meta-[4] and ortho-[5]xylenes form soluble sulphonates and can be separated from the sulphuric acid solution.[6] Dilute the solution with water, neutralize with barium carbonate, filter off the barium sulphate, concentrate the filtrate by evaporation, and divide into two parts. Set one portion away and allow the barium salts to crystallize. Treat the remainder with a slight excess of sodium carbonated, and concentrate by evaporation. After standing

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[1]Ident. of Pure Organic Comp., Mulliken, p. 202.
[2]Am. Chem. Pharm., Vol. LXIX., p. 162.
Ibid, Vol. CLXXXVI., p. 331.
Journ. Prakt. Pharm., Vol. LXI., p. 74.
Ibid, Vol. LXX., p. 300.
[3]Treatise on Chem., Roscoe and Scharlemmer, Vol. III., part 4, p. 388.
Coal Tar and Ammonia, Lunge, p. 156.
Berichte der deut. Chem., Gesel, Vol. IX., p. 405.
[4]Ibid, Vol. X., p. 1010.
[5]Ibid, Vol. CLIII., p. 265.
[6]Treatise on Chem., Vol. III., part 4, p. 388.

for several hours large prism shaped crystals of sodium ortho-xylene sulphonate[1] $C_6H_2(CH_3)_2SO_3Na + 5H_2O$, crystallize out. A portion of the crystals were treated with hydrochloric acid, nitrated with fuming nitric acid crystallized from alcohol and the melting point taken.[2]

Since sodium meta-xylene sulphonate does not crystallize it was separated from the filtered solution by means of HCl, nitrated, and the melting point of the nitro compound taken.

The portion of the xylene which did not form a sulphonate was washed with water and sodium hydrate redistilled, and a few drops nitrated[1] as follows: Boiled with 1 c.c. of fuming nitric acid and 2 c.c. concentrated sulphuric acid, for 1 minute. Poured into cold water, filter, wash with alcohol. These crystals were clusters of white needles, which were trinitro paraxylene $C_6H(CH_3)_2(NO_2)_3$.[2]

The amounts of para- meta- and ortho-xylenes in xylene have been variously estimated. Usually, however, meta-xylene has the largest percentage and ortho- the smallest. Levinstein[5] has found in various samples of crude xylene:

Paraxylene	3—10%
Metaxylene	70—87%
Orthoxylene	2—15%
Paraffine	3—10%

When a mixture of the three xylenes is treated with bromine containing 1% of iodine, they are converted into the tetra-bromo-xylenes, $C_6Br_4(CH_3)_2$. If

[1]Treatise on Chem., Vol. III., part 4, p. 388.
[2]Ident. Pure Org. Comp., Mulliken, p. 203.
[3]Ident. Pure Org. Comp., Mulliken, p. 202.
[4]Berichte der deut. Chem., Gesel, Vol. X., 1010; Xi., 22.
[5]Ibid, Vol. XVII., p. 444.

heated to 160°-170° this yields the tetra-brom-phthalic acids quantitatively; $C_6Br_4(CH_3)_2+6Br_2+4H_2O=C_6Br_4(CO_2H)_2+12HBr$. Since these can be readily separated, the composition of the original mixture can be determined in this way.[1]

Fraction 3b when refractionated yielded 20 c.c. between 136°-142°. This is 4% of fraction I or .27% of the tar. Of this amount para-xylene represents .05%.

Cumene, $C_6H_3(CH_3)_3$.

An effort to determine the presence of trimethyl benzene resulted in a sulphonated product of distillate 3b, but since little is known of cumene, no satisfactory qualitative tests were applied. Cumene has been found in crude petroleum.[2]

Ferric ferrocyanide was found to have come over in the low boiling fractions of distillate I. and separated out of the dilute sulphuric acid solution. Its presence was not detected above fraction 3b.

Fractions II. and III., 160°-245°, 6.82% sp. gr. .9219.

500 c.c. was refractionated as follows:

Fraction	Range in Temp.	Amt. in C. C.
1. 100°	160°C	67
2. 160°	200°C	181
3. 200°	211°C	102
4. 215°	235°C	95
5. 235°	245°C	14
Residue above	245°C	37

Refractioning.

Fraction 1.		
a. 100°	120°C	9
b. 120°	130°C	16.5
c. 130°	150°C	22.5
d. 150°	16$°C	10.5
Above	160°C	8.5

[1]Compt. rend., Vol. CI., p. 1218.
[2]Am. Chem. Pharm., Vol. CCXXXIV., p. 89.
Berichte der Chem., 1876, p. 256.

Fraction 1c was treated for xylene and gave an addition of 5 c.c. crude xylene, making a total of .32% in the tar.

Naphthalene, $C_{10}H_8$, m. p. 81°.

Fractions 3, 4 and 5 were cooled to 4°C for 24 hours. A white crystalline solid separated out. This was filtered while cold, the oil pressed out, purified with sulphuric acid and manganese dioxide and recrystallized from alcohol. Its melting point was found to be 78°-80°C, and its boiling point 218°C. .1 gram of the crystals was treated with picric acid and the melting point of the long hair like needles separating out, was found to be 150.5°, which is that of naphthalene picrate, $C_{10}H_4C_6H_4(NO_3)_2O$[1]. Fractions II. and III. yielded 1.28% of naphthalene, the greater part coming over in fraction 4, which was almost entirely solid.

Phenol, C_6H_5OH, m. p. 42, b. p. 183.

Fraction III. was agitated with sodium hydroxide, filtered, neutralized with sulphuric acid and tested for phenols with ferric chloride. There was no trace of a coloration. Nor could any deep colored nitro compound be produced. The solution was also unaffected by bromine water.

Fraction IV., 245°-265°, 9.53% sp. gr. .9624.

500 c.c. was redistilled and divided into four fractions:

Fraction	Range in Temp.	Amt. in C. C.
1. 200°	215°C	79
2. 215°	235°C	258
3. 235°	245°C	54
4. 245°	260°C	46
Residue above	260°C	73

[1]Ident. of Pure Org. Comp., Mulliken, p. 200.

Fractions 1, 2 and 3 were cooled to 4°C, the naphthalene pressed out while cold, purified and crystallized. Yield, 1.08%.

Fraction V., 265°-295°, 9.16%, sp. gr. .9795.

500 c. c. was redistilled as in the preceding fractions.

Fraction	Range in Temp.	Amt. in C. C.
1. 200°	215°	15
2. 215°	235°	160
3. 235°	245°	118
4. 245°	260°	95
5. 260°	295°	85

.79% of naphthalene was gotten from fractions 1, 2 and 3. This makes a total yield of naphthalene from fractions II., III., IV. and V. of 3.13%.

Fraction VI., 295°-335°, 13.38%, .9940 sp. gr.

A crystalline solid settled out of fraction VI., which was of a greenish fluorescent color very unlike naphthalene. It was thoroughly shaken up and 500 c.c. was redistilled.

Fraction	Range in Temp.	Amt. in C. C.
1. 200°	215°C	10
2. 215°	235°C	25
3. 235°	245°C	20
4. 245°	260°C	93
5. 260°	290°C	148
6. 290°	300°C	27
7. 300°	320°C	47
8. 320°	340°C	26
9. 340°	360°C	14
Residue above	360°	90

A very small amount of naphthalene separated out of fraction 1.

Anthracene, $C_{14}H_{10}$, m. p. 213°, b. p. 351°.

The greenish, fluorescent solid appeared in fractions 7, 8 and 9. These fractions were cooled in ice at o°C

for 24 hours and filtered while cold. The crystals were pressed out, freed from oil and dried at 100°, redistilled and purified with NaOH. .1 gram was oxidized with chromic acid and the residue crystallized from alcohol. The melting point of the compound was found to be 279°-280°, which is that of anthraquinone.[1] To further verify the test the anthraquinone was converted into oxanthranol. When anthracene is thus oxydised it yields anthraquinone. Yield of anthracene from fraction VI., 0.26%.

Fraction VII., 235°-265°, 1.0342 sp. gr., 13.57%.

Fraction VII. was treated as the other distillates.

Fraction	Range in Temp.	Amt. in C. C.
1. 260°	290°C	100
2. 290°	300°C	98
3. 300°	320°C	93
4. 320°	340°C	60
5. 340°	360°C	100
6. 360°	365°C	13
Residue above	365°C	36

Fractions 2, 3, 4 and 5 were cooled to 0°C for 24 hours and filtered while cold. The anthracene was purified as in VI. Yield, .434%, making a total of .694% of anthracene in the tar. The amount of anthracene oil from which it crystallized was 27.9% of the tar.

Paraffins.

The high boiling fractions from 240°-365° when sulphonated left a residue which was clear and oily. It was carefully washed free from sulphuric acid and the sulphonates and dried over calcium chloride. The index of refraction was found to be but slightly above that of fraction VI. of the gas oil. The sulphonation was repeated and the index of refraction lowered

.0115, which made it almost the same as that of the gas oil. In a discussion of the sulphonation test, Dean and Bateman[1] have this to say: "If a fraction from the distillation of creosote oil be treated under proper conditions with concentrated sulphuric acid it will be converted into a mixture of sulphonic acids, which will readily dissolve in water. If, however, there are paraffin bodies present they will not be attacked to the same degree as the aromatic hydrocarbons and when the products of the sulphonation are treated with water the paraffin compounds will remain as residual oil." Applying this test the tar seemed to show the presence of unchanged aliphatic compounds of gas oil.

The following gives the results of the chemical analysis in tabulated form.

Water	6.61%
Ferric ferrocyanide	Trace
Carbon bisulphide	None
Thiophene	Trace
Benzene	.22%
Toluene	.11%
Orthoxylene	
Meta-xylene	
Para-xylene	.05%
Cumene	Trace
Phenol	None
Naphthalene	3.13%
Anthracene oil (270°-365°)	27.9 %
Anthracene	.69%
Paraffine	High %
Residue	21.45%

This analysis is not completed, since an effort has been made to discover the presence of only the more common aromatic hydrocarbons.

The residue which remains after the six fractions of the tar have been taken is a very black tar which resembles "No. 24" of coal tar distillates. It is more

[1]Circular 112, Forest Service Series.

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brittle, however, and has a much less range of elasticity. It becomes very brashy at a freezing temperature, and liquifies at the temperature of a warm summer day. This would preclude its use as a paving material, unless mixed with coal tar.

A series of experiments were conducted under the observation of the author at the Nashville Chemical Company, with mixtures of coal tar and water gas tar above 360°. A very good grade of tar was produced, but the tendency to separate out on the part of the unchanged paraffn gave some trouble. A high percentage of water was also found to be present, and the difficulties of distillation were greater than in coal tar. There seemed to be present a rather large quantity of free carbon in the form of lamp black. This lowered the utility of the tar very greatly. Nevertheless, the increasing manufacture of water gas and the demand for a substitute for coal tar made by the present method may finally lead to the commercial utilization of water gas residue. When the process of its production has been so perfected that the residue is always uniform, and the danger of producing a high percentage of lamp black has been removed, then it will become marketable.

CONCLUSIONS

1. The gas oil used in the process of carburetting water gas undergoes a chemical and physical change when converted into water gas tar.

2. Some of the oil goes through the process unchanged, or nearly so, and may be detected in the distillation above 250°C.

3. No phenols were found in the fractions below 260°C.

4. Benzene, Toluene, Xylene, Naphthalene and Anthracene were found in the tar.

5. The tar varies in density and constituency. This is governed, first, by the gas oil used in the run; second, by the method in which the process of water gas formation is conducted.

6. Because of a low range of flexibility and elasticity of the pitch the tar is not practicable as a substitute for coal tar in the preparation of paving compounds, but may be of some utility when mixed with it.

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